Supporting information

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Can a Single Water Molecule Affect the Hydrogen Abstraction Reaction of HO_2+NO_2 under Tropospheric Conditions?

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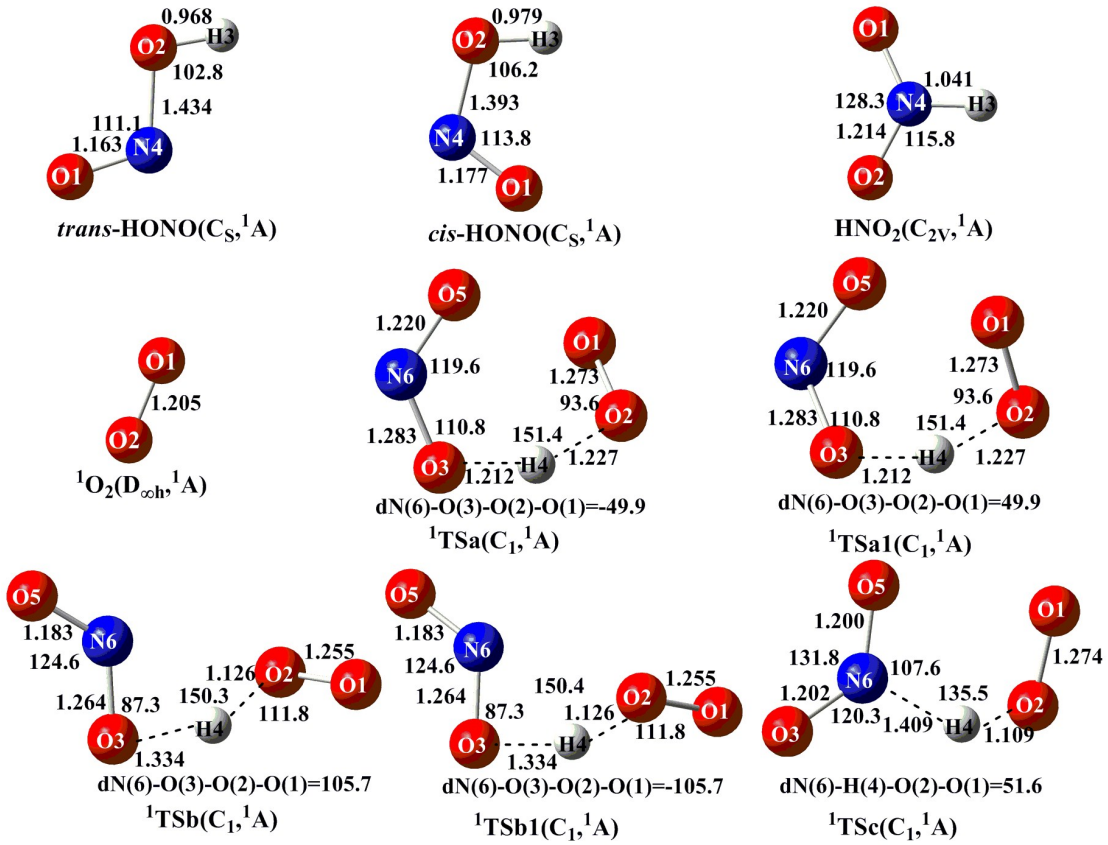

Fig. S1 Geometrical parameters for the singlet naked reaction of HO_2+NO_2 optimized at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level of theory

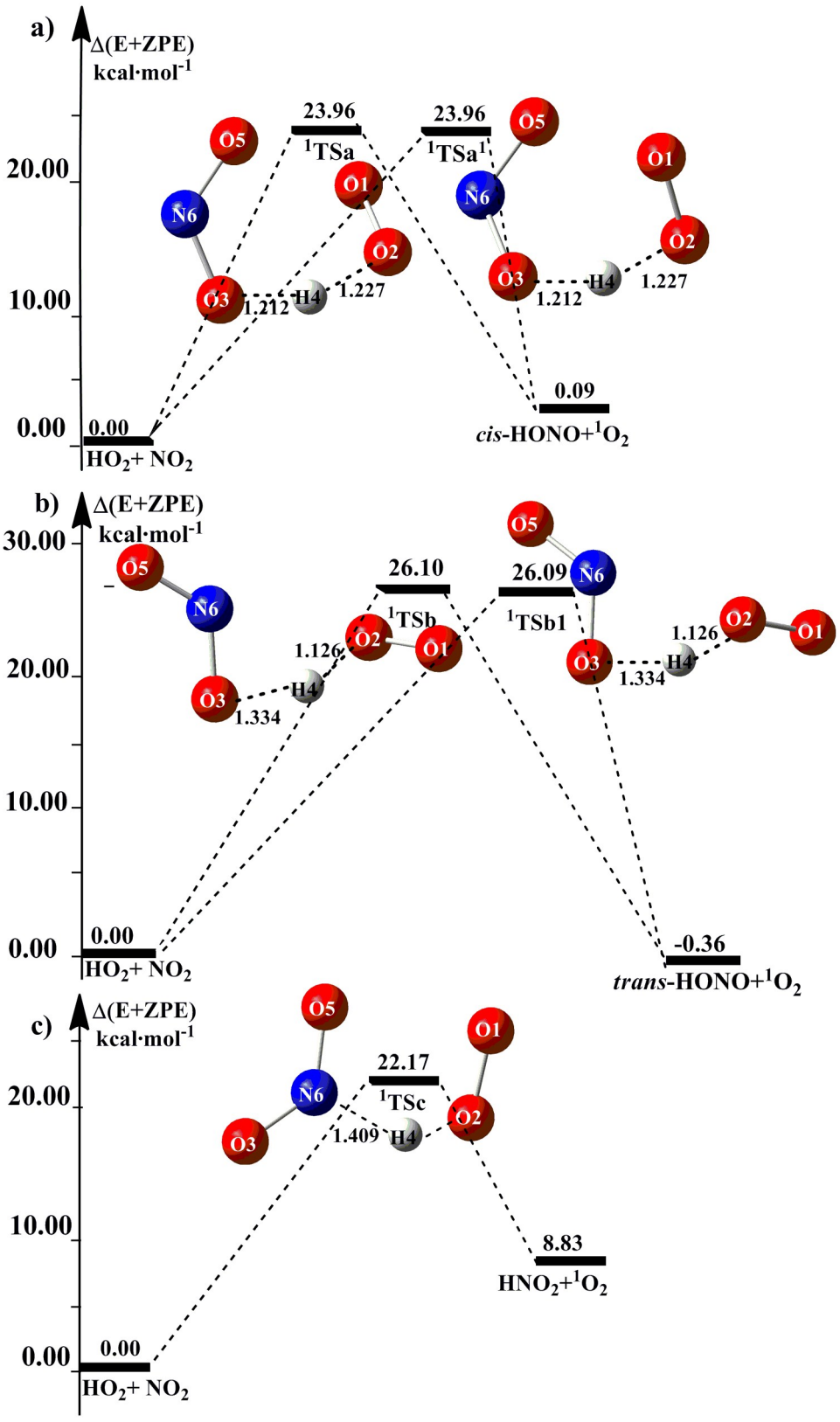

Fig. S2 Schematic energy diagram of the formation of (a)cis-HONO+$^1O_2$; (b) trans-HONO+$^1O_2$ and (c)HNO_2+$^1O_2$ involved in the singlet reaction of HO_2 + NO_2 Energies (kcal·mol^{-1}) computed at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level include zero-point energy correction.

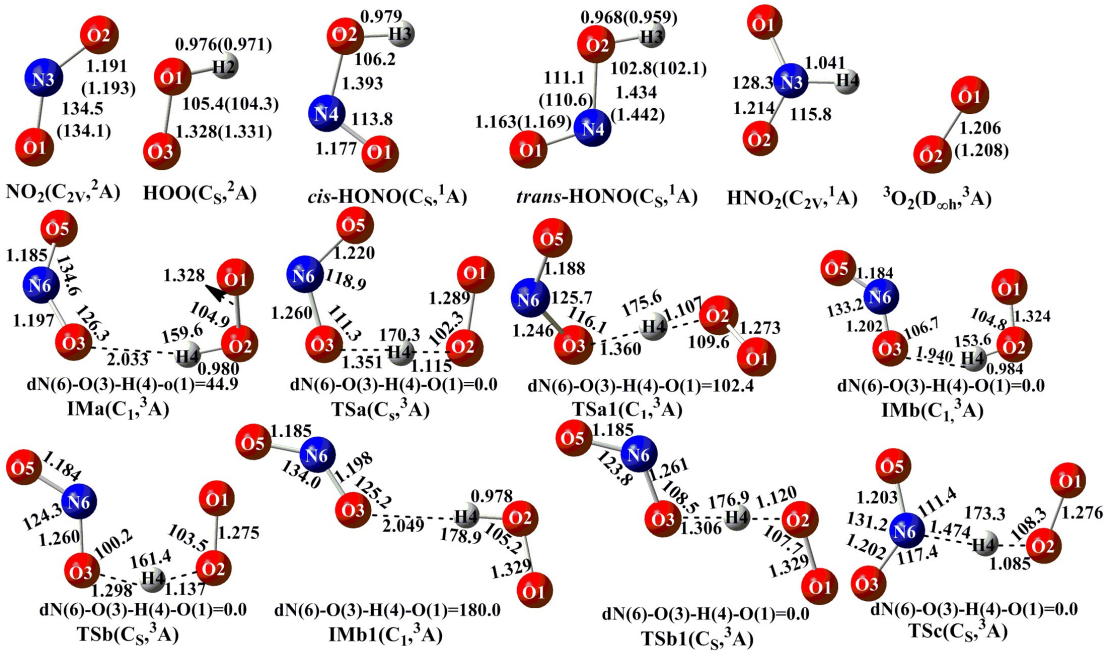

Fig. S3 Geometrical parameters for the triplet naked reaction of HO_2+NO_2 optimized at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level of theory

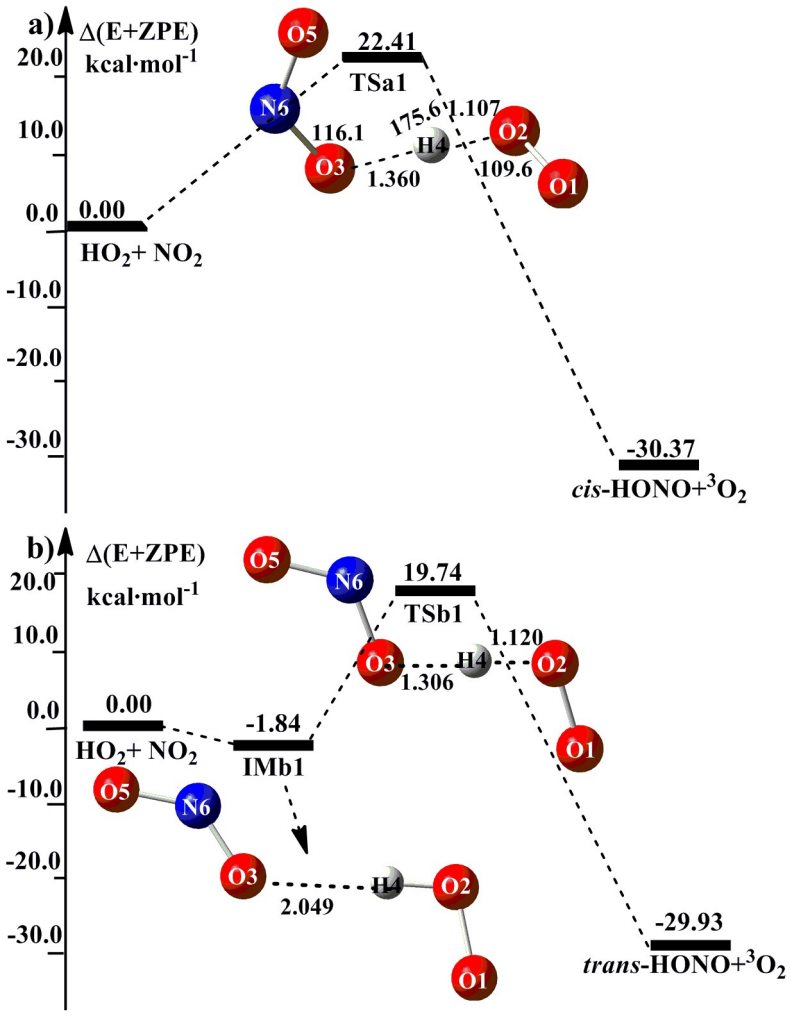

Fig. S4 Less favorable schematic energy diagram of the formation of (a)cis-HONO+$^3O_2$; (b) trans-HONO+$^3O_2$ involved in the triplet reaction of HO_2 + NO_2 Energies (kcal·mol^{-1}) computed at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level include zero-point energy correction.

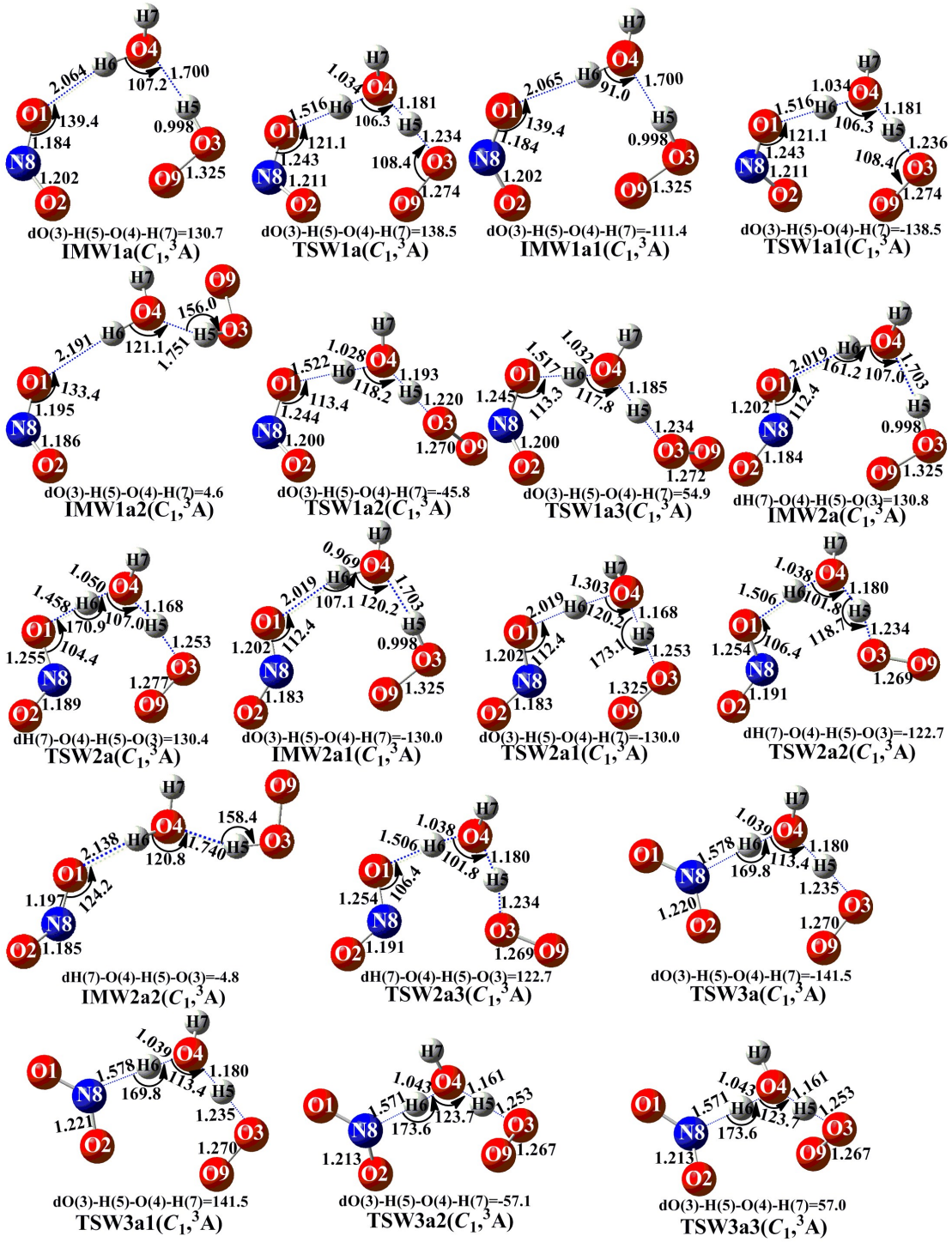

Fig S5 The geometrical structures of the optimized transitions state, intermediates, and complexes involving the $H_2O\cdots HO_2+NO_2$ reaction

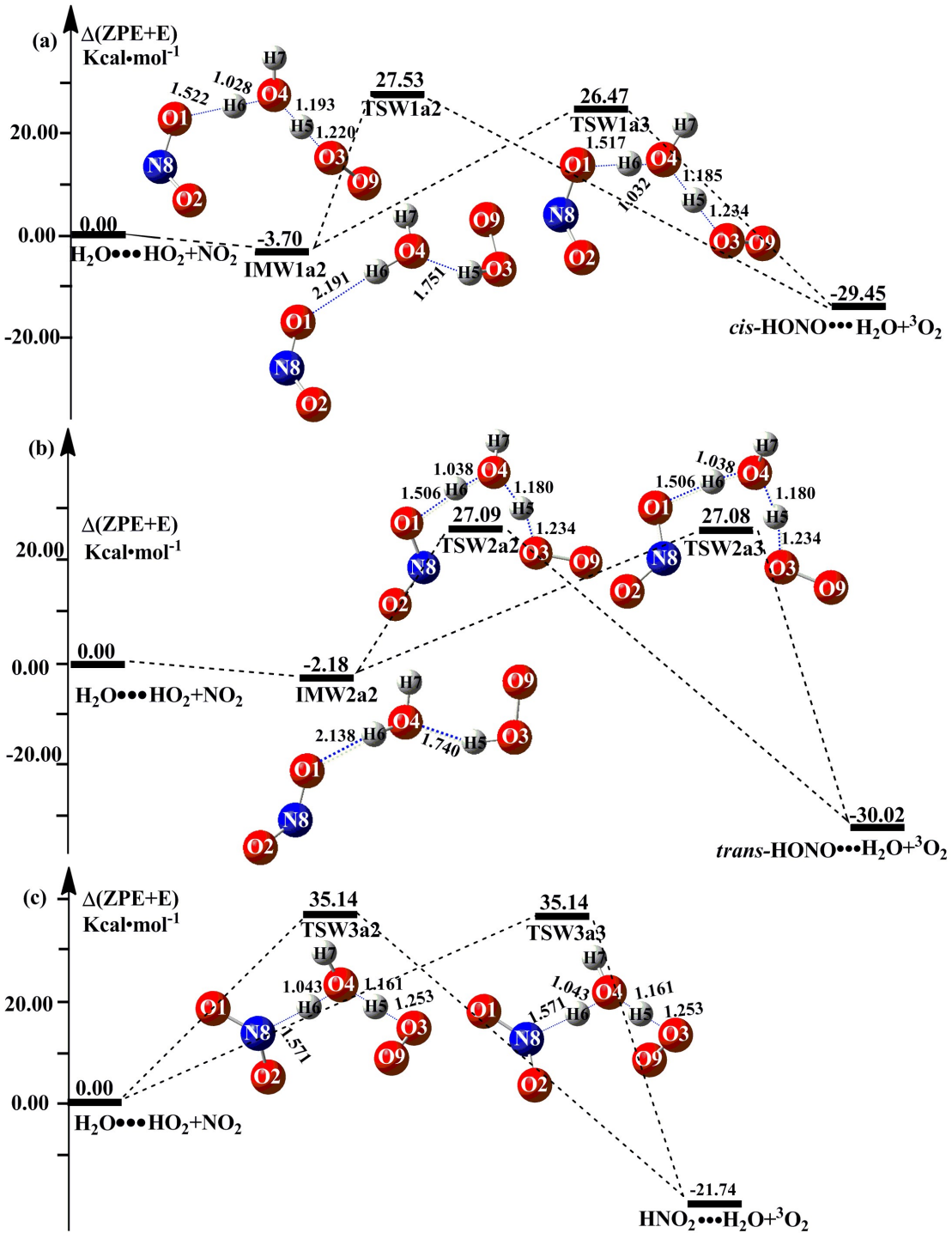

Fig S6 Less favorable schematic energy diagrams of the formation of (a) cis-HONO···H_2O+$^3O_2$; (b) trans-HONO···H_2O+$^3O_2$ and (c) HNO_2···H_2O+$^3O_2$ in the H_2O···HO_2+NO_2 reaction

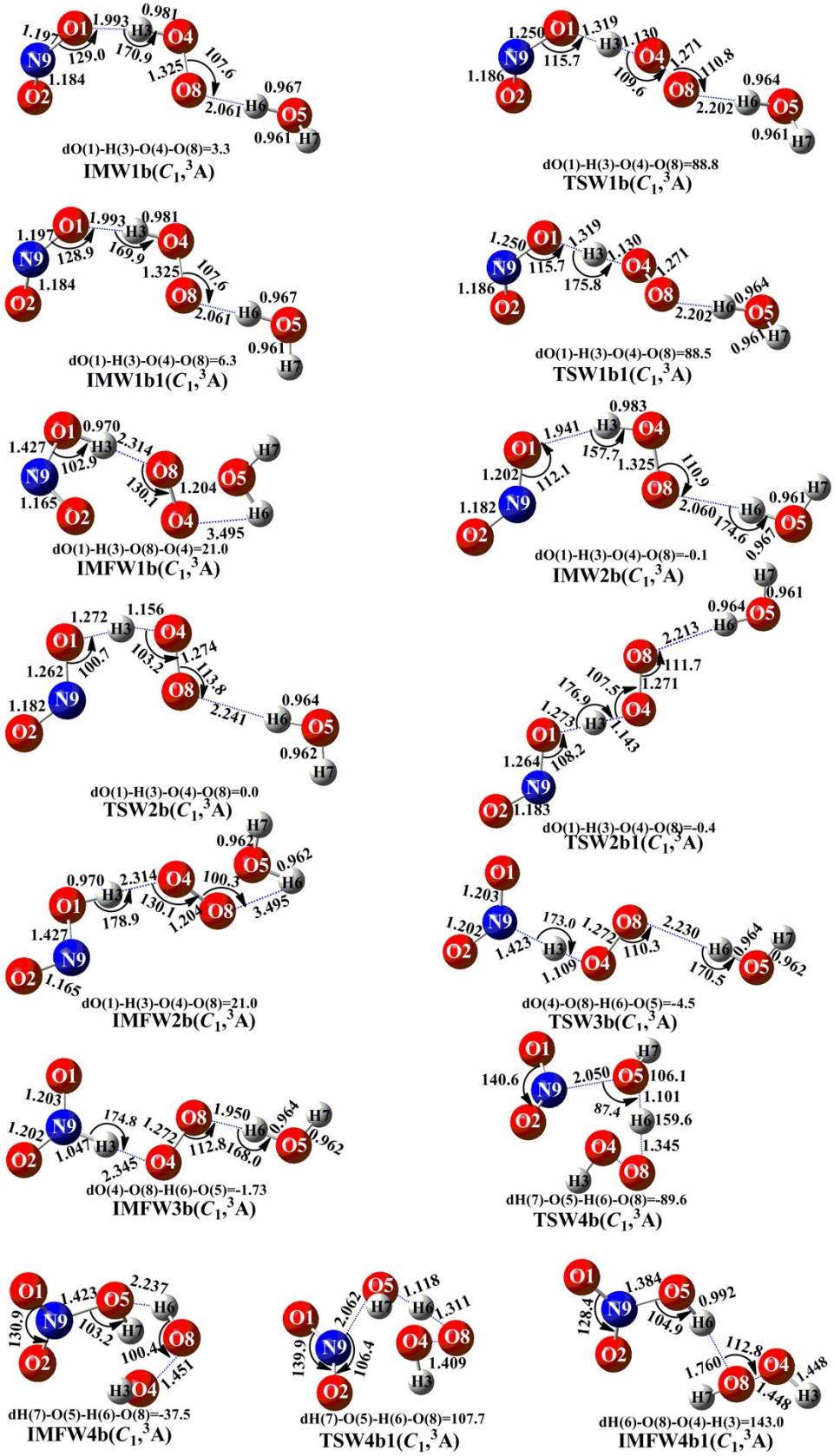

Fig S7 The geometrical structures of the optimized transitions state, intermediates, and complexes involving the $HO_2\cdots H_2O+NO_2$ reaction and Schematic energy diagrams of the formation of $HNO_3+H_2O_2$ in the $H_2O\cdots HO_2+NO_2$ reaction

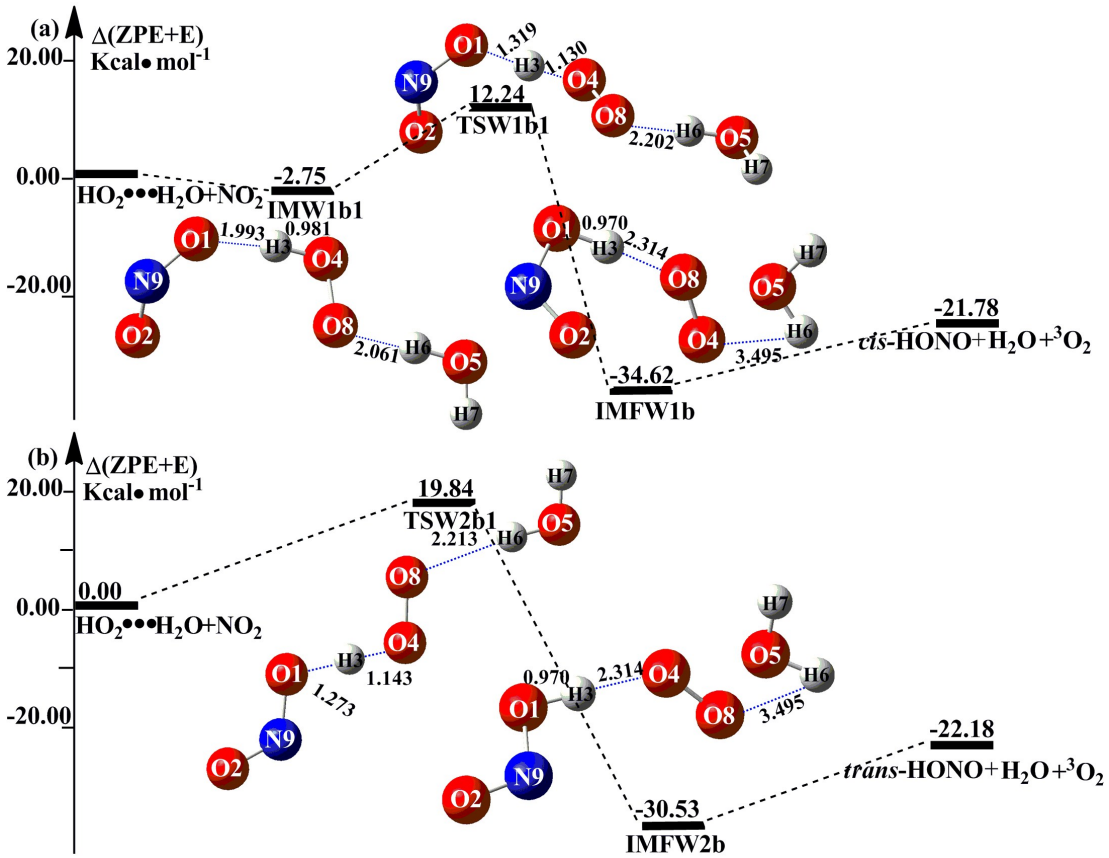

Fig S8 Less favorable schematic energy diagrams of the formation of (a) cis-HONO+H_2O+$^3O_2$; (b) trans-HONO+H_2O+$^3O_2$ in the HO_2···H_2O+NO_2 reaction

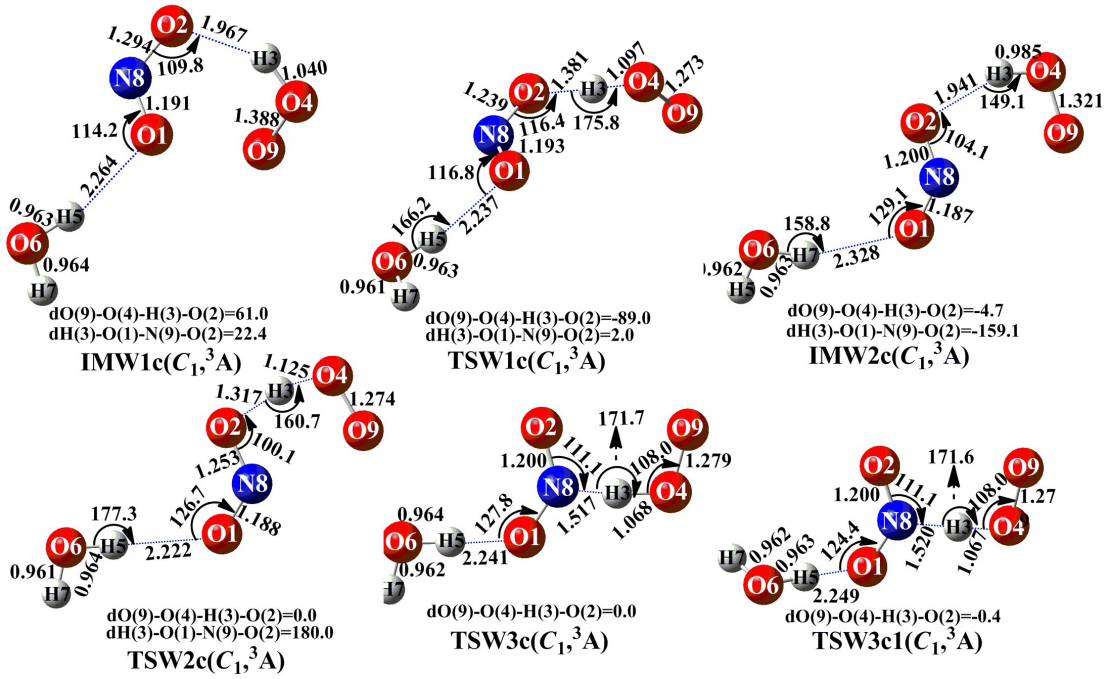

Fig. S9 The geometrical structures of the optimized transitions state, intermediates, and complexes involving the $NO_2\cdots H_2O+HO_2$ reaction

Table S1. *T*1 diagnostic values for the species that involved in the title reactions of NO_2 + HO_2 without and with a water molecule

Species	T_1	Species	T_1	Species	T_1
***cis*-HONO**	0.0115	**$^3O_2$**	0.0176	**IMW1b1**	0.0274
***trans*-HONO**	0.0117	**H_2O•••HO_2**	0.0210	**TSW1b1**	0.0400
HNO_2	0.0203	**IMW1a**	0.0214	**IMFW1b**	0.0185
$^1O_2$	0.0152	**TSW1a**	0.0330	**IMW2b**	0.0267
NO_2	0.0244	**IMW1a1**	0.0214	**TSW2b**	0.0477
H_2O	0.0101	**TSW1a1**	0.0330	**TSW2b1**	0.0469
HO_2	0.0301	**IMW1a2**	0.0273	**IMFW2b**	0.0250
^{1}TSa	0.0194	**TSW1a2**	0.0360	**TSW3b**	0.0364
^{1}TSa1	0.0194	**TSW1a3**	0.0358	**IMFW3b**	0.0210
^{1}TSb	0.0193	**IMW2a**	0.0261	**NO_2•••H_2O**	0.0231
^{1}TSb1	0.0149	**TSW2a**	0.0417	**IMW1c**	0.0273
^{1}TSc	0.0476	**IMW2a1**	0.0261	**TSWIc**	0.0392
IMa	0.0298	**TSW2a1**	0.0412	**IMW2c**	0.0255
TSa	0.0369	**TSW2a2**	0.0408	**TSW2c**	0.0481
TSa1	0.0354	**IMW2a2**	0.0266	**TSW3c**	0.0420
IMb	0.0294	**TSW2a3**	0.0419	**TSW3c1**	0.0418
TSb	0.0394	**TSW3a**	0.0329	**TSW4b**	0.0383
IMb1	0.0288	**TSW3a1**	0.0328	**IMFW4b**	0.0170
TSb1	0.0390	**TSW3a2**	0.0325	**TSW4b1**	0.0377
TSc	0.0312	**TSW3a3**	0.0325	**IMFW4b1**	0.0169
***cis*-HONO••• H_2O**	0.0189	**HO2•••H2O**	0.0245		
***trans*-HONO•••H_2O**	0.0188	**IMW1b**	0.0275		
HONO•••H_2O	0.0180	**TSW1b**	0.0400		

Table S2 Zero-point energy (ZPE, in kcal·mol^{-1}), entropies (S in cal·mol^{-1}·k^{-1}), relative energies (ΔE and $\Delta(E+$ ZPE) in kcal·mol^{-1}), enthalpies ($\Delta H(298)$ in kcal·mol^{-1}), and free energies ($\Delta G(298)$ in kcal·mol^{-1}) for the $HO_2 + NO_2$ reaction [a]

Species	ZPE	S	ΔE	$\Delta(E+$ZPE)	$\Delta H(298)$	$\Delta G(298)$
HO_2+NO_2	14.32	111.98	0.00	0.00	0.00	0.00
^{1}TSa	13.98	73.97	26.44	26.10	-5.36	5.97
^{1}TSa1	13.98	73.97	26.44	26.09	-5.36	5.97
Trans-HONO+$^1O_2$	14.93	106.31	-0.96	-0.36	-4.10	-2.41
^{1}TSb	13.94	69.87	24.35	23.96	-5.78	6.77
^{1}TSb1	13.94	69.87	24.35	23.96	-5.79	6.77
Cis-HONO+$^1O_2$	14.88	106.11	-0.46	0.09	-4.19	-2.44
^{1}TSc	14.14	73.02	22.35	22.17	-5.26	6.35
$HNO_2+^1O_2$	15.98	105.24	7.17	8.83	-3.22	-1.21
IMa	15.29	92.47	-2.89	-1.92	-2.78	3.04
TSa	13.00	75.42	23.73	22.41	-6.35	4.55
TSa1	12.84	80.72	13.59	12.11	-6.18	3.14
Trans - HONO+$^3O_2$	14.94	108.39	-30.99	-30.37	-3.82	-2.76
IMb	15.50	82.19	-3.81	-2.64	-3.34	5.55
TSb	13.62	76.16	9.82	9.11	-5.69	4.99
IMb1	15.24	86.40	-2.76	-1.84	-3.32	4.31
TSb1	12.81	81.47	21.27	19.75	-6.14	2.95
Cis -HONO+$^3O_2$	14.89	108.19	-30.49	-29.93	-3.92	-2.79
TSc	13.08	79.98	9.60	8.35	-6.01	3.53
$HNO_2+^3O_2$	16.00	107.33	-22.86	-21.18	-2.95	-1.56

[a] ZPE and S values obtained at B3LYP/aug -cc-pVTZ level. The energy values are obtained at CCSD(T)/aug -cc-pVTZ level whereas the H and G corrections are taken from the B3LYP/aug -cc-pVTZ values.

Table S3 Zero point energy (ZPE, in kcal·mol^{-1}), entropies (S in cal·mol^{-1}·k^{-1}), relative energies (ΔE and $\Delta(E+$ ZPE*)* in kcal·mol^{-1}), enthalpies ($\Delta H(298)$ in kcal·mol^{-1}), and free energies ($\Delta G(298)$ in kcal·mol^{-1}) for water-catalyzed the main channel of $HO_2 + NO_2$ reaction occurring through $H_2O\cdots HO_2 + NO_2$ reaction

Species	ZPE	S	ΔE	$\Delta(E+\text{ZPE})$	$\Delta H(298)$	$\Delta G(298)$
$H_2O\bullet\bullet\bullet HO_2+NO_2$	30.62	128.99	0.00	0.00	0.00	0.00
IMW1a	30.87	99.56	-1.15	-0.90	0.20	8.98
TSW1a	28.55	91.28	23.86	21.79	-2.97	8.27
IMW1a1	30.86	99.56	-1.22	-0.98	0.20	8.98
TSW1a1	28.55	91.29	23.86	21.79	-2.97	8.27
IMW1a2	30.76	113.80	-1.87	-1.73	0.90	5.43
TSW1a2	27.97	97.79	30.19	27.53	-3.16	6.14
TSW1a3	27.75	97.63	29.34	26.47	-3.38	5.97
cis-HONO•••H2O+$^3O_2$	29.94	126.45	-28.77	-29.45	-0.40	0.36
IMW2a	31.16	101.84	-3.78	-3.24	0.89	8.99
TSW2a	28.79	89.31	17.39	15.55	-2.82	9.01
IMW2a1	31.17	101.85	-3.84	-3.29	0.90	8.99
TSW2a1	29.00	90.12	17.42	15.80	-2.53	9.13
TSW2a2	28.37	93.88	29.34	27.09	-2.96	7.51
IMW2a2	30.80	105.38	-2.35	-2.18	0.34	7.38
TSW2a3	28.38	93.88	29.33	27.08	-2.95	7.51
trans-HONO•••H2O+$^3O_2$	29.80	130.32	-29.19	-30.02	-0.25	-0.65
TSW3a	27.95	93.26	33.69	31.01	-3.38	7.27
TSW3a1	27.56	99.37	38.21	35.14	-3.56	5.27
TSW3a2	27.95	93.26	33.67	30.99	-3.38	7.27
TSW3a3	27.56	99.36	38.21	35.14	-3.56	5.28
HONO•••H2O+$^3O_2$	30.40	133.81	-21.52	-21.74	0.42	-1.02

[a] ZPE and S values obtained at B3LYP/aug -cc-pVTZ level. The energy values are obtained at CCSD(T)/aug -cc-pVTZ level whereas the H and G corrections are taken from the B3LYP/aug -cc-pVTZ value.

Table S4 Zero point energy (ZPE, in kcal·mol^{-1}), entropies (S in cal·mol^{-1}·k^{-1}), relative energies (ΔE and $\Delta(E+$ ZPE*)* in kcal·mol^{-1}), enthalpies ($\Delta H(298)$ in kcal·mol^{-1}), and free energies ($\Delta G(298)$ in kcal·mol^{-1}) for water-catalyzed the main channel of $HO_2 + NO_2$ reaction occurring through $HO_2\cdots H_2O + NO_2$ reaction

Species	ZPE	S	ΔE	$\Delta(E$+ZPE)	$\Delta H(298)$	$\Delta G(298)$
HO_2•••H_2O+NO_2	29.55	138.10	0.00	0.00	0.00	0.00
IMW1b	30.06	117.20	-3.15	-2.65	0.96	7.16
TSW1b	27.10	108.10	14.70	12.25	-2.68	6.27
IMW1b1	29.97	112.10	-3.17	-2.75	0.36	8.10
TSW1b1	27.08	108.70	14.70	12.24	-2.68	6.08
IMFW1b	30.23	107.74	-35.30	-34.62	-0.12	8.92
cis-HONO+H_2O+$^3O_2$	28.22	153.3	-27.24	-21.78	-1.67	-6.21
IMW2b	30.25	113.70	-4.41	-3.71	1.03	8.29
TSW2b	27.77	106.10	11.30	9.52	-2.18	7.34
TSW2b1	30.14	109.10	-4.30	-3.72	0.42	9.06
IMFW2b	29.04	109.64	-30.02	-30.53	-0.94	7.54
trans-HONO+H_2O+$^3O_2$	28.27	153.50	-27.73	-22.18	-1.57	-6.17
TSW3b	27.24	105.90	10.13	7.81	-2.48	7.12
IMFW3b	30.52	94.42	-22.62	-21.65	-0.76	12.26
HONO+H_2O+$^3O_2$	29.33	152.4	-19.60	-13.17	-0.69	-4.97
TSW4b	31.37	80.17	24.90	26.73	-0.52	16.73
IMFW4b	33.87	94.29	-22.35	-18.03	3.07	16.12
TSW4b1	31.10	80.65	26.31	27.85	-0.78	16.34
IMFW4b1	34.50	89.06	-27.02	-22.08	3.27	17.89
HNO_3+H_2O_2	33.01	119.40	-17.59	-14.12	1.77	7.35

[a] ZPE and S values obtained at B3LYP/aug -cc-pVTZ level. The energy values are obtained at CCSD(T)/aug -cc-pVTZ level whereas the H and G corrections are taken from the B3LYP/aug -cc-pVTZ value.

Table S5 Zero point energy (ZPE, in kcal·mol^{-1}), entropies (S in cal·mol^{-1}·k^{-1}), relative energies (ΔE and $\Delta(E+$ ZPE*)* in kcal·mol^{-1}), enthalpies ($\Delta H(298)$ in kcal·mol^{-1}), and free energies ($\Delta G(298)$ in kcal·mol^{-1}) for water-catalyzed the main channel of HO_2 + NO_2 reaction occurring through $NO_2\cdots H_2O+HO_2$ reaction

Species	ZPE	S	ΔE	$\Delta(E+ZPE)$	$\Delta H(298)$	$\Delta G(298)$
NO_2•••H_2O+HO_2	28.52	143.80	0.00	0.00	0.00	0.00
IMW1c	30.76	113.80	-9.91	-7.68	1.79	10.73
TSWIc	27.16	109.90	12.97	11.60	-2.00	8.10
cis-HONO•••$H_2O+{}^3O_2$	29.94	126.40	-36.81	-35.39	0.49	5.66
IMW2c	29.66	110.00	-3.63	-2.49	0.73	10.80
TSW2c	27.97	103.70	8.88	8.33	-1.54	10.42
trans-HONO•••$H_2O+{}^3O_2$	29.80	130.30	-37.23	-35.96	0.65	4.65
TSW3c	27.52	110.80	10.39	9.38	-1.64	8.19
TSW3c1	27.56	110.00	10.31	9.35	-1.61	8.45
HONO•••$H_2O+{}^3O_2$	30.40	133.80	-29.56	-27.68	1.31	4.28

[a] ZPE and S values obtained at B3LYP/aug -cc-pVTZ level. The energy values are obtained at CCSD(T)/aug -cc-pVTZ level whereas the H and G corrections are taken from the B3LYP/aug -cc-pVTZ value.

Table S6 Rate constants ($cm^3 \cdot molecules^{-1} \cdot s^{-1}$) for main reaction of the $HO_2 + NO_2$ reaction within the temperature range of 240.0−425.0 K

T/K	k_{R1}	k_{R2}	k_{R3}	k_R
240	2.54E-17	1.95E-15	3.66E-15	5.64E-15
250	2.28E-17	1.57E-15	2.94E-15	4.53E-15
278	1.80E-17	9.39E-16	1.75E-15	2.71E-15
288	1.68E-17	8.07E-16	1.49E-15	2.31E-15
298	1.59E-17	7.02E-16	1.29E-15	2.01E-15
308	1.51E-17	6.18E-16	1.13E-15	1.76E-15
325	1.40E-17	5.06E-16	9.22E-16	1.44E-15
375	1.21E-17	3.15E-16	5.73E-16	9.00E-16
425	1.13E-17	2.26E-16	4.09E-16	6.46E-16

k_{R1} is the rate constant of Channel R1; k_{R2} is the rate constant of Channel R2, and k_{R3} is the rate constant of Channel R3.

Table S7 Rate constants ($cm^3 \cdot molecules^{-1} \cdot s^{-1}$) for main reaction of the $HO_2 + NO_2$ reaction occurring through $H_2O \cdots HO_2 + NO_2$ reaction within the temperature range of 240.0−425.0K

T/K	k_{RW1a1}	k_{RW1a2}	k_{RW1a3}	k_{RW1a4}	k_{RW1a}	k_{RW2a1}	k_{RW2a2}	k_{RW2a3}
240	9.56E-28	9.56E-27	3.59E-38	6.94E-31	1.05E-26	1.73E-22	8.33E-32	8.33E-32
250	2.52E-27	2.52E-26	4.30E-37	1.42E-30	2.77E-26	3.94E-22	2.70E-31	2.70E-31
278	4.00E-26	4.00E-25	1.98E-34	1.37E-29	4.40E-25	3.81E-21	8.76E-30	8.76E-30
288	1.06E-25	1.06E-24	1.36E-33	3.31E-29	1.17E-24	8.26E-21	3.11E-29	3.11E-29
298	2.78E-25	2.78E-24	8.33E-33	8.20E-29	3.06E-24	1.74E-20	1.10E-28	1.10E-28
308	7.12E-25	7.11E-24	4.57E-32	2.07E-28	7.82E-24	3.58E-20	3.77E-28	3.77E-28
325	3.29E-24	3.29E-23	6.56E-31	1.01E-27	3.62E-23	1.13E-19	2.86E-27	2.86E-27
375	1.74E-22	1.74E-21	4.35E-28	8.57E-26	1.91E-21	2.12E-18	5.53E-25	5.53E-25
425	4.39E-21	4.39E-20	6.61E-26	3.85E-24	4.83E-20	2.22E-17	3.92E-23	3.92E-23

T/K	k_{RW2a4}	k_{RW2a}	k_{RW3a1}	k_{RW3a2}	k_{RW3a3}	k_{RW3a4}	k_{RW3a}
240	3.13E-30	1.73E-22	4.46E-32	4.60E-32	3.13E-34	3.14E-34	9.12E-32
250	8.93E-30	3.94E-22	1.14E-31	1.18E-31	9.40E-34	9.45E-34	2.34E-31
278	1.95E-28	3.81E-21	1.80E-30	1.85E-30	2.35E-32	2.36E-32	3.70E-30
288	6.05E-28	8.26E-21	5.02E-30	5.16E-30	7.73E-32	7.77E-32	1.03E-29
298	1.87E-27	1.74E-20	1.42E-29	1.46E-29	2.59E-31	2.60E-31	2.93E-29
308	5.73E-27	3.58E-20	4.06E-29	4.18E-29	8.79E-31	8.83E-31	8.41E-29
325	3.65E-26	1.13E-19	2.44E-28	2.51E-28	7.06E-30	7.09E-30	5.09E-28
375	4.87E-24	2.12E-18	3.79E-26	3.88E-26	2.45E-27	2.46E-27	8.16E-26
425	2.71E-22	2.22E-17	2.98E-24	3.04E-24	3.76E-25	3.78E-25	6.77E-24

k_{RW1a} ($k_{RW1a} = k_{RW1a1} + k_{RW1a2} + k_{RW1a3} + k_{RW1a4}$) is the rate constant of Channel RW1a; k_{RW2a} ($k_{RW2a} = k_{RW2a1} + k_{RW2a2} + k_{RW2a3} + k_{RW2a4}$) is the rate constant of Channel RW2a, and k_{RW3a} ($k_{RW3a} = k_{RW3a1} + k_{RW3a2} + k_{RW3a3} + k_{RW3a4}$) is the rate constant of Channel RW3a.

Table S8 Rate constants ($cm^3 \cdot molecules^{-1} \cdot s^{-1}$) for main reaction of the $HO_2 + NO_2$ reaction occurring through $HO_2 \cdots H_2O + NO_2$ reaction within the temperature range of 240.0−425.0K

T/K	k_{RW1b1}	k_{RW1b2}	k_{RW1b}	k_{RW2b1}	k_{RW2b2}	k_{RW2b}	k_{RW3b}
240	8.46E-14	2.66E-14	1.11E-13	1.98E-12	1.35E-09	1.35E-09	5.42E-12
250	9.71E-14	3.73E-14	1.34E-13	2.37E-12	6.14E-10	6.16E-10	8.30E-12
278	1.91E-13	1.06E-13	2.97E-13	4.47E-12	1.76E-10	1.80E-10	2.58E-11
288	2.61E-13	1.58E-13	4.20E-13	5.80E-12	1.47E-10	1.53E-10	3.78E-11
298	3.60E-13	2.38E-13	5.99E-13	7.62E-12	1.35E-10	1.43E-10	5.46E-11
308	5.18E-13	3.58E-13	8.78E-13	1.01E-11	1.33E-10	1.43E-10	7.79E-11
325	9.51E-13	7.18E-13	1.67E-12	1.63E-11	1.47E-10	1.63E-10	1.39E-10
375	5.42E-12	5.01E-12	1.05E-11	6.56E-11	2.93E-10	3.59E-10	6.17E-10
425	2.53E-11	2.75E-11	5.33E-11	2.31E-10	6.63E-10	8.94E-10	2.14E-09
T/K	k_{RW4b1}	k_{RW4b2}	k_{RW4b}				
240	1.75E-34	2.85E-35	2.04E-34				
250	1.41E-33	2.42E-34	1.65E-33				
278	2.25E-31	4.48E-32	2.70E-31				
288	1.09E-30	2.28E-31	1.32E-30				
298	4.75E-30	1.05E-30	5.80E-30				
308	1.89E-29	4.37E-30	2.33E-29				
325	1.63E-28	4.07E-29	2.04E-28				
375	3.03E-26	9.22E-27	3.95E-26				
425	1.69E-24	6.04E-25	2.29E-24				

k_{RW1b} (k_{RW1b}= k_{RW1b1}+ k_{RW1b2}) is the rate constant of Channel RW1b; k_{RW2b} (k_{RW2b}= k_{RW2b1}+ k_{RW2b2})is the rate constant of Channel RW2b; k_{RW3b} is the rate constant of Channel RW3b, and k_{RW4} (k_{RW4}= k_{RW4b1}+ k_{RW4b2}) is the rate constant of Channel RW4.

Table S9 Rate constants ($cm^3 \cdot molecules^{-1} \cdot s^{-1}$) for main reaction of the $HO_2 + NO_2$ reaction occurring through $NO_2 \cdots H_2O + HO_2$ reaction within the temperature range of 240.0−425.0 K

T	k_{RW1c}	k_{RW2c}	k_{RW3c1}	k_{RW3c2}	k_{RW3c}
240	1.27E-15	1.39E-13	1.30E-14	9.44E-15	2.25E-14
250	2.25E-15	1.92E-13	2.85E-14	2.07E-14	4.91E-14
278	1.15E-14	4.85E-13	1.94E-13	1.40E-13	3.34E-13
288	2.03E-14	6.74E-13	3.54E-13	2.55E-13	6.09E-13
298	3.52E-14	9.32E-13	6.23E-13	4.47E-13	1.07E-12
308	5.99E-14	1.28E-12	1.06E-12	7.59E-13	1.82E-12
325	1.41E-13	2.16E-12	2.44E-12	1.74E-12	4.19E-12
375	1.28E-12	8.59E-12	1.90E-11	1.35E-11	3.25E-11
425	7.65E-12	2.76E-11	9.55E-11	6.72E-11	1.63E-10

k_{RW1c} is the rate constant of Channel RW1c; k_{RW2c} is the rate constant of Channel RW2c, and k_{RW3c} ($k_{RW3c}= k_{RW3c1}+ k_{RW3c2}$) is the rate constant of Channel RW3c.